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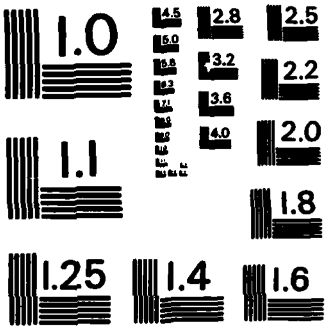
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SPECTROSCOPY OF NAPHTHALENE IN SIMPLE MOLECULAR LIQUIDS

by

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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

Optical spectra of the first excited singlet state $({}^1B_{1u})$ of naphthalene in cryogenic molecular hydrocarbon alkane and alkene liquids (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, 1-C_4H_8) have been obtained and are discussed in terms of the solute solvent intermolecular interaction. Data include gas to liquid shifts, Franck-Condon shifts, line widths for absorption and emission, and their temperature dependence. Naphthalene line widths and their temperature dependences and Franck-Condon shifts are smaller than those found for benzene but the gas to liquid shifts for both systems are quite similar. Based on these results and the comparison with similar benzene data, the ground and excited state Lennard-Jones type potential curves for naphthalene/solvent interactions can be generated. The main conclusions are that naphthalene has a stronger interaction with the solvent than does benzene, the interaction scales with solvent polarizability, and the change in cavity radius upon excitation is greater for benzene than for naphthalene. Lifetime data have also been obtained for the naphthalene fluorescence. At low temperature, the liquid state lifetime for fluorescence is roughly the same as that found in the low pressure gas (~300 ns). A small temperature dependence is characterized for these low concentration solutions leading to an activation energy for naphthalene collision induced intersystem crossing of ~100 cm^{-1}. The excimer formation and monomer regeneration mechanism reported for benzene is also observed in naphthalene C_3H_6 and C_3H_8 solutions but it is of much less importance to the overall kinetics.

ABSTRACT

Optical spectra of the first excited singlet state ($^1B_{1u}$) of naphthalene in cryogenic molecular hydrocarbon alkane and alkene liquids (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, 1-C_4H_8) have been obtained and are discussed in terms of the solute solvent intermolecular interaction. Data include gas to liquid shifts, Franck-Condon shifts, line widths for absorption and emission, and their temperature dependence. Naphthalene line widths and their temperature dependences and Franck-Condon shifts are smaller than those found for benzene but the gas to liquid shifts for both systems are quite similar. Based on these results and the comparison with similar benzene data, the ground and excited state Lennard-Jones type potential curves for naphthalene/solvent interactions can be generated. The main conclusions are that naphthalene has a stronger interaction with the solvent than does benzene, the interaction scales with solvent polarizability, and the change in cavity radius upon excitation is greater for benzene than for naphthalene. Lifetime data have also been obtained for the naphthalene fluorescence. At low temperature, the liquid state lifetime for fluorescence is roughly the same as that found in the low pressure gas (~300 ns). A small temperature dependence is characterized for these low concentration solutions leading to an activation energy for naphthalene collision induced intersystem crossing of ~100 cm^{-1}. The excimer formation and monomer regeneration mechanism reported for benzene is also observed in naphthalene C_3H_6 and C_3H_8 solutions but it is of much less importance to the overall kinetics.

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I. INTRODUCTION

Spectroscopic and lifetime studies of probe molecules in cryogenic small molecule liquid solvents have been demonstrated to yield useful information concerning the microstructure and microdynamics of the liquid state.[1,2,3] Electronic absorption and emission data include gas to liquid shifts, Frank-Condon shifts, line widths and their temperature dependences. These results can be employed in conjunction with calculations to study the intermolecular solvent/solute potential surface near its equilibrium separation distance. The fluorescence lifetimes trace the fate of solute molecules in the liquid at low concentration. Comparing these with the lifetimes of molecules in the low pressure gas phase and in room temperature liquids, information on the radiationless transitions in the condensed phase can be extracted. In addition, some qualitative understanding of long time (tens of nanoseconds) solvent cage dynamics can arise from such investigations.

In this paper we report the absorption and emission data for the first excited singlet state ($^1B_{3u}$) of naphthalene in cryogenic hydrocarbon liquids. These data are analyzed through comparison with those obtained for benzene in the same solvent and, consequently, information on the naphthalene solvent intermolecular potential is generated. Model potential calculations can be fitted to these data based on a Lennard-Jones formulation. It is suggested that the ground state solute-solvent interaction is stronger for naphthalene than for benzene in the same solvent. The excited state potential is also deeper for naphthalene than for benzene. However, such a simple potential model fails to represent the line width behavior.

The lifetime of the naphthalene $^1B_{3u}$ state fluorescence in various cryogenic liquids is also reported. The results are consistent with a model in which the (isoenergetic) intersystem crossing from the zero point levels of the $^1B_{3u}$ state to the lowest triplet state ($^3B_{2u}$) of naphthalene is saturated due to the dense set of vibronic triplet states. Thus, for this pathway the radiationless relaxation is temperature (solvent collision) independent. However, collisions may induce intersystem crossing to the much less dense manifold of high triplet states. The formation of naphthalene excimers is less probable than the formation of benzene excimers; this observation is rationalized based on solvent solute interactions, monomer shape, and monomer diffusion.

II. EXPERIMENTAL

Sample preparation and instrumental techniques have been described in other papers from our laboratory.[1,3,4] It has been found that impurities such as β-methylnaphthalene can cause difficulties with fluorescence spectra[5] and lifetime studies especially in the crystal. Consequently, potassium treatment of the naphthalene (Fisher Gold Label) was employed to reduce the level of such contaminants.[6] Although zone refining is a further step that helps remove impurities such as anthracene,[7] this procedure was omitted because it was felt unnecessary in these experiments. The naphthalene was further purified by vacuum sublimation following the potassium treatment. Since naphthalene has a low vapor pressure and a high melting temperature, the deposition process is somewhat revised compared to that which has been previously described. A 150 ml stainless steel bottle was added to the manifold, filled with $C_{10}H_8$ vapor and kept at ~10°C higher than the temperature of the naphthalene sample. Solvent was then passed through this chamber in the deposition process. The actual concentrations thus generated are very close to the calculated values expected based on vapor pressure ratios and oscillator strength.

III. RESULTS

The absorption and emission spectra of the first excited singlet state of naphthalene have been obtained in CH_4, C_2H_4, C_2H_6, C_3H_8, C_3H_6, and $1\text{-}C_4H_8$. Fig. 1 shows the spectra of 5 ppm naphthalene in C_2H_6 at 90K. Assignment of features in the absorption is made through comparison with data from the molecular jet experiment.[8] The assignment of the emission features is consistent with that of Hollas.[9] Table I gives the absorption and emission line widths of naphthalene in various solvents at the same temperature. Also shown in Table I are the absorption and emission line widths of benzene for comparison. It is clear from Table I that the absorption and emission line widths of naphthalene in all solvents studied are narrower than those found for benzene under the same conditions. The gas to liquid shifts for naphthalene are listed in Table II along with the Franck-Condon shifts for the various solvents. The values for benzene are also included in Table II for comparison. It is found that while the gas to liquid shifts for naphthalene and benzene are quite comparable, the Franck-Condon shifts for naphthalene are smaller by a factor of two than those of benzene.

A study of the lifetime of naphthalene in these solvents as a function of temperature and concentration has been performed and the results are given in Fig. 2-6. The relatively low solubility of naphthalene in these solvents prevents the study of high concentrations (greater than 20 ppm). Except in C_3H_6 and C_3H_8 solvents, it is found that a change in concentration from 0.1 to 10 ppm does not result in a noticeable reduction of the lifetime. In C_3H_6 and C_3H_8 solvents, however, due to the large liquid temperature ranges obtainable and low viscosity of these solvents, a small but consistently reproducible increase in the lifetime at high temperature can be observed as shown in Fig. 5 and 6. This is likely due to the breakup of a small population of excimers at these higher temperatures. Note, however, that the regeneration of monomers from the excimer typically occurs near 150 to 170K indicating that solvent behavior may play a fundamental role in this overall kinetic process.[1,2]

IV. DISCUSSION

The spectroscopic data for naphthalene in cryogenic hydrocarbon liquids show the same main features observed for benzene: nearly temperature independent absorption line widths, emission line widths which broaden to the low energy side as temperature is increased, a low temperature, low concentration lifetime approaching that found in the low pressure gas phase, and a gradual increase in the (unimolecular) nonradiative rate as temperature is increased. As in the case of benzene, the naphthalene data could be used to obtain information on the reduced ground state potential surface by applying McRae's formula[10] and making various approximations, assuming all the appropriate oscillator strengths and frequencies are known. Even the benzene analysis, however, required a base or standard solution (cyclohexane) upon which to set parameters.[1] Since the trends and general features of the naphthalene and benzene data sets are so similar, benzene actually serves as a more realistic and reliable model system than even the calculations.

On the other hand, the naphthalene excited state kinetics seem more temperature and concentration independent over the ranges followed in these studies. This indicates that the self-quenching mechanism, so central to the benzene solution kinetics, is less of a factor for naphthalene. Thus, the solution kinetics in the ensuing discussion will not be dealt with in a fashion parallel to that already presented for benzene.[3]

A. Intermolecular Potentials

As shown for benzene,[1] solute molecular spectra can be usefully employed in the study of solute solvent intermolecular interactions and potentials. For the sake of clarity and comparison, the benzene data and analysis procedure will be reviewed. In absorption, the vertical Franck-Condon process projects the ground state equilibrium position (for a given temperature) onto the excited state intermolecular potential surface. Liquid state emission spectra, on the other hand, probe the corresponding part of the ground state intermolecular potential from the excited state equilibrium configuration (for a given temperature). Since it is likely that the intermolecular potential consists of a steep repulsive part and a relatively flat long range attractive part,[11] the data for both the naphthalene and benzene systems require an excited state solvent/solute cage that is smaller than the ground state one. One then approximates the difference between the ground and excited state potential minima in the liquid as the absorption 0_0^0 transition energy. The (typically negative) gas to liquid shift is obtained by subtracting this value from the gas phase 0_0^0 transition energy. Under these assumptions, the difference between the absorption and emission gas to liquid shifts, that is the Franck-Condon shift, can be regarded as the energy difference between the ground state potential minimum and the ground state potential energy vertically projected from the potential minimum of the excited state intermolecular potential. The Franck-Condon shifts in this approximate analysis for benzene thus are assumed to contain information on the repulsive part of the ground state intermolecular potential.

In the previous benzene analysis,[1] an identical form for the reduced ground state intermolecular coordinate was assumed for all solvents and a standard solvent, namely cyclohexane, with an averaged intermolecular distance for the ground state potential minimum of 3Å, was employed to calculate the potential as a function of cavity size and percent of change in cavity size upon excitation.[10]

Since not all the transition frequencies and oscillator strengths are known for naphthalene, a similar calculation would not be very reliable. However, the comparison between naphthalene and benzene is not only reliable, it is also useful, physically meaningful, and capable of generating a qualitative picture of the intermolecular interactions at least to some extent.

For the sake of comparison, consider that the intermolecular interactions can be modeled by a simple Lennard-Jones potential written in the following form for the ground (") and excited (') states,

$$E''(r) = 4\varepsilon''\left[\left(\frac{\sigma''}{r}\right)^{12} - \left(\frac{\sigma''}{r}\right)^{6}\right] \tag{1}$$

$$E'(r) = 4\varepsilon'\left[\left(\frac{\sigma'}{r}\right)^{12} - \left(\frac{\sigma'}{r}\right)^{6}\right] + E_o. \tag{2}$$

While, as we show, the powers 12-6 are not central to this analysis, the general form of the potential is; a more complicated three or four parameter potential would not be useable with the data. In eq. (1) and (2) ε and σ are parameters for the well depth and equilibrium position, respectively. Since upon excitation, well depth and position are expected to change, is it assumed that $\sigma' \neq \sigma''$ and $\varepsilon'' \neq \varepsilon'$. Consequently, the model begins with two equations and six unknowns. The absorption and emission data provide that,

$$E'(r''_{min}) - E''(r''_{min}) = E_{abs} \tag{3}$$

$$E'(r'_{min}) - E''(r'_{min}) = E_{em} \tag{4}$$

in which E_{abs} and E_{em} are the observed absorption and emission 0_0^0 frequencies of the solute in the liquid and r''_{min} and r'_{min} are the minimum potential (equilibrium) positions of the ground and excited states, respectively. If the ratio of well depths is also taken as $\gamma = \frac{\sigma'}{\sigma''}$, eqs. (1) and (2) and (3) and (4) can be combined to give

$$(\gamma^{12} - 2\gamma^{6})\varepsilon' \quad + \quad \varepsilon'' = \Delta_{gl} \tag{5}$$

$$\varepsilon' + [(\frac{1}{\gamma})^{6}]\,\varepsilon'' = \Delta_{FC} - \Delta_{gl}, \tag{6}$$

in which Δ_{gl} is the gas to liquid shift and Δ_{FC} is the Franck-Condon shift. In order to solve these equations, further assumptions involving γ need to be made. First, $\gamma \leq 1$, that is, the excited state molecule interacts more strongly with the solvent cage than does the ground state molecule. This relation has been determined for C_6H_6 (C_6D_6),[1] $C_4N_2H_2$,[12] and C_7H_8.[13] Second, $\varepsilon_{solvent} \leq \varepsilon'' \leq \varepsilon_{solute}$; that is, the energy parameter for the ground state Lennard-Jones interaction potential between two different molecules (solute and solvent) is assumed to have a value between the values of the solute-solute and solvent-solvent parameters, ε_{solute} and $\varepsilon_{solvent}$. One can use the first assumption to generate a series of ε' and ε'' and employ the second assumption to confine the range of γ to an "appropriate" value. Thereby, specific potentials can be simultaneously constructed for the ground and excited state.

Application of the above approximate scheme to the $C_{10}H_8/C_3H_8$ and C_6D_6/C_3H_8 systems results in a range of γ for each system. Although there is a region of energy for which $\epsilon''_{C_{10}H_8}$ and $\epsilon''_{C_6D_6}$ overlap each other, the cavity size ratio γ does not overlap and gives a larger value for $C_{10}H_8/C_3H_8$ than C_6D_6/C_3H_8. Thus, upon excitation the model predicts that the change in cavity size for $C_{10}H_8$ is smaller than for C_6D_6 in the propane solvent. This interesting result can be correlated with the polarizability data for C_6D_6 and $C_{10}H_8$. According to the previous benzene results[1] and recent observations for the toluene system,[13] the solute-solvent interaction scales quite accurately with the solvent and solute polarizability and is independent of their dipole moment. The ratio of the excited to ground state polarizability (α'/α'') for these two solute molecules indicates a smaller value for $C_{10}H_8$ (~ 1.14)[14] than for C_6D_6 (~ 1.2)[15]: hence $\gamma_{C_{10}H_8} > \gamma_{C_6D_6}$. The smaller spectral line width for $C_{10}H_8$ in comparison to C_6D_6, which is evident in all solvents (Table I), also supports a smaller cavity change upon $C_{10}H_8$ excitation.

In order to compare the intermolecular interaction for $C_{10}H_8$ and C_6D_6 solvent systems, a set of ($\gamma, \epsilon'', \epsilon'$) for each system must be selected. As an example, the middle value for each bracket is picked for ϵ''. Although this is a rather arbitrary choice, data sets thus generated are well fitted to the above polarizability argument; that is, a large polarizability corresponds to a large interaction potential energy minimum (ϵ), and a small energy increment $(\frac{\epsilon'-\epsilon''}{\epsilon''})$ corresponds to a small polarizability increment $(\frac{\alpha'-\alpha''}{\alpha''})$ for $C_{10}H_8$. Once ϵ'' and ϵ' are decided, the Franck-Condon shifts for the individual ground and excited state wells can be determined.

As a consequence of these Lennard-Jones potentials, the molecular excited state has a larger Franck-Condon shift than the ground state, a result which is at variance with the previous benzene analysis assumption. This is a direct consequence of the larger γ values and relatively small values for ϵ' and ϵ'' in the Lennard-Jones potential model. If the intermolecular potential were truly of this form for both states (as will be shown below it must not be, however), the previous potential well for C_6D_6 in cryogenic liquids[1] should reflect the attractive part of the excited state rather than the repulsive part of the ground state.

Similar comparison between C_6D_6 and $C_{10}H_8$ in solvents other than C_3H_8 further support the polarizability dependent trends and larger excited state Franck-Condon shifts than ground state ones. Moreover, the cavity ratio $\gamma(=\frac{\sigma'}{\sigma''})$ for $C_{10}H_8$ (or C_6D_6) in various solvents is found to scale with polarizability. As solvent polarizability increases, the solvent cavity becomes smaller upon excitation (smaller γ) in agreement with the previous ab initio calculation for C_6D_6.[1] However, the absolute ratio γ is larger for the Lennard-Jones model than for the ab initio one and the Lennard-Jones model is also more sensitive to changes in cavity size and solvent polarizability. The reasons for this lie in a steep r dependence and relatively shallow ϵ' and ϵ'' for the Lennard-Jones potentials.

The Lennard-Jones model approach has two advantages: comparison between many different systems is possible as it serves to organize a good deal of data; and it can provide some insight, in principle, into the molecular excited state interactions.

There are, however, two serious problems with the Lennard-Jones approach. First, it fails to predict the proper spectroscopic line widths based on a simple Boltzmann population in the ground and excited state wells. According to the Lennard-Jones model the emission lines should be broader than the absorption lines; the opposite is observed. Second, the absorption lines are predicted to be temperature dependent not the emission features. These two failures are quite important as they suggest the shapes and relative depths of the two wells are incorrectly modeled.

These two contradictions suggest that the restrictions of well depth ($\varepsilon''_{\text{solute}} \geq \varepsilon'' \geq \varepsilon''_{\text{solvent}}$) and shape (12-6 powers) should be released. For simplicity the 12-6 power restriction was relaxed for the molecular excited state, which modifies eq. (2) in the following manner:

$$E' = \left\{ \left[\frac{m}{n}\right]^{\frac{n}{n-m}} - \left[\frac{m}{n}\right]^{\frac{m}{n-m}} \right\}^{-1} \varepsilon'\left[\left(\frac{\sigma'}{r}\right)^{n} - \left(\frac{\sigma'}{r}\right)^{m}\right] + E_{o} \qquad (7)$$

in which n and m are the powers for the repulsive and attractive parts of the potential, respectively.

Several n-m pairs, including 12-1, 12-3, 24-3, 10-4, 9-3, and 6-1 have been tested at different potential energies. The results show that none of these pairs satisfies the line width value and its temperature response simultaneously, although all other experimental observations can be well fit. Such a disagreement between calculated and observed results suggests that a more complicated intermolecular interaction than a simple two parameter Lennard-Jones type is required for these liquids. More complicated three parameter potentials, however, would not be useful in data comparison and organization.

This Lennard-Jones approach is useful in comparing data from different systems but only presents part of the overall interaction picture.

B. Lifetimes

The study of naphthalene lifetimes in cryogenic liquids shows that at low temperature ($T<100K$) the observed lifetimes approach those that of the dilute low pressure gas phase value. This indicates that the quantum yields for fluorescence in these two quite different environments are almost the same. Collisions between naphthalene and the surrounding solvent cage molecules must be weak and ineffective in enhancing intersystem crossing. Two factors contribute to this observation: low kinetic energy of the solvent molecules generating a more rigid solvation cage structure and a dense triplet vibronic manifold from the lowest triplet state ($^3B_{2u}$) at the $^1B_{3u}$ energy. Benzene behaves in a comparable fashion once the kinetics are extrapolated to infinite dilution to suppress the excimer formation-monomer regeneration mechanism. Table III contains these comparative results.

The decay rate for naphthalene as a function of temperature in $1\text{-}C_4H_8$ can be written as

$$k = 3.0 \times 10^6 + 7.2 \times 10^6 \, e^{\frac{-114}{KT}} \quad . \tag{8}$$

The temperature independent part of eq. (8) yields a lifetime of ~300 ns which is close to the reported lifetime in the gas phase.[16] The second term can be attributed to collisionally induced intersystem crossing.[17] The activation energy associated with this term (~100 cm^{-1}) is roughly twice as large as that found for benzene. The temperature independent part of the benzene decay rate in very dilute solutions is also consistent with the gas phase collision free lifetime (~200 ns C_6D_6 and ~100 ns C_6H_6).[18] This discussion suggests that the temperature independent part of both decay rates is governed by an intramolecular relaxation process and that the temperature dependent part is governed by collisionally induced intersystem crossing. This latter effect increases with temperature and is more important for naphthalene than benzene as indicated by the activation energies.

It is known that the energy difference between the first excited singlet state and lowest triplet state of naphthalene is ~10000 cm^{-1} [19]; this difference for benzene[20] is ~8600 cm^{-1}. Thus, a dense set of lowest triplet vibronic states can be expected isoenergetic with the first excited singlet states of these systems. The dense triplet manifolds drive the irreversible nonradiative processes in the collision free single molecule (large molecule limit). In low temperature liquids, weak collisions with the solvent molecules do not increase the coupling between these two electronic states; that is, fluorescence quenching through this channel has been saturated.[21] However, the higher energy triplet states do not have a dense manifold of states isoenergtic with the first excited singlet state zero point level. This circumstance, of course, corresponds to the small molecule limit.[22] In this situation, collisions with the surrounding solvent shell molecules can move the less dense manifold of upper triplet states into and out of resonance with the lowest singlet state zero point level and thus alter the nonradiative intersystem crossing rates. One predicts that the smaller the singlet-triplet separation is, the larger the activation energy associated with this process will be.[17] It is found that the energy difference between the first excited singlet state and the next lowest triplet state is ~300 cm^{-1} for naphthalene [32020 cm^{-1} ($^1B_{3u}$) - 31700 cm^{-1} ($^3B_{3u}$)][19] and ~1650 cm^{-1} for benzene [38289 cm^{-1} ($^1B_{2u}$) - 36650 cm^{-1} ($^3E_{1u}$)].[20] Therefore, the activation energy for collisionally induced intersystem crossing is expected to be larger for naphthalene than for benzene, as is observed.

The concentration independence of the lifetime of naphthalene in cryogenic solvents would indicate a non-dominant excimer formation decay rate. There are two possible general explanations for this observation. First, the just discussed large activation energy (~100 cm^{-1}) for intersystem crossing implies a large change in lifetime as the temperature is increased. Thus, naphthalene intersystem crossing could actively compete with the nonradiative rate due to excimer formation. Secondly, the probability of excimer formation for naphthalene solutions may simply be smaller than for benzene solutions. There are several factors that can contribute to the overall probability of excimer formation. The larger size of naphthalene may mean slower diffusion in solution although the long lifetime could compensate for this. There are also fewer ways to form a naphthalene excimer than a benzene excimer. Energetics could also be a factor for the probability of excimer formation. Since naphthalene has a stronger interaction with the solvent than does benzene, the naphthalene-solvent cage is more stable and this may affect excimer formation; the collisional cross section for excimer formation thus becomes smaller and the excimer may have a shorter lifetime.

Nonetheless, a small but consistently reproducible increase in the lifetime of naphthalene in C_3H_6 and C_3H_8 solvents around 150 to 170K, as shown in Figs. 5 and 6, indicates some formation of excimers. These particular solvents show the effect due to their wide liquid state range as a function of temperature and low viscosity. The qualitative behavior in these systems is quite similar to that found for benzene.

Finally, an extrapolation of the lifetime of naphthalene from low temperature to room temperature yields a value of ~140 ns at ~300K. This is higher than the usually reported lifetime for naphthalene fluorescence at room temperature (120 ns).[22] The lower room temperature measured value can be attributed to a sudden increase of the intersystem crossing rate at an excess singlet state energy of 1000 cm^{-1}.[16] The same situation was found for benzene for which the anomaly appears at ~2500 cm^{-1} above the vibrationless level of the $^1B_{2u}$ state.[20]

V. SUMMARY AND CONCLUSIONS

Spectroscopic data for naphthalene in cryogenic hydrocarbon solutions have been analyzed and compared to those data obtained from benzene. The smaller naphthalene Franck-Condon shifts and line widths suggest that upon excitation the solute/solvent intermolecular interaction changes less in the case of naphthalene solutions than in the case of benzene solutions. On the other hand, the naphthalene solvent interaction is stronger in both states than the benzene solvent ineraction. This trend scales well with solvent and solute polarizabilities. The Lennard-Jones model used to extract these ideas, however, does not predict the proper line widths or their temperature dependences. Thus, while useful, the Lennard-Jones type potential is not quantitatively correct for these systems.

Lifetime data show that in low temperature liquids, naphthalene has a fluorescence decay rate close to the value for the isolated free molecule; this is also true for benzene. An analysis of the lifetime of these two systems indicates that the temperature dependence of the decay rate is due to collisionally induced intersystem crossing to the next lower triplet state.

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TABLE I

Absorption and emission line widths of naphthalene and benzene in various solvents. (in cm^{-1}, error ±20 cm^{-1})

	Solvent	Temperature (K)	Absorption Line Width (cm^{-1})
Naphthalene	C_2H_6	150	142
	C_2H_4	165	149
	C_3H_8	150	142
Benzene	C_2H_6	150	190
	C_2H_4	165	208
	C_3H_8	150	190

	Solvent	Temperature (K)	Emission Line Width (cm^{-1})
Naphthalene	C_2H_6	90	110
		150	146
		180	183
	C_2H_4	110	146
	C_3H_8	90	140
		150	182
Benzene	C_2H_6	90	172
		150	245
		180	331
	C_2H_4	110	238
	C_3H_8	90	227
		150	300

TABLE II

Gas to liquid shifts in absorption and Franck-Condon shifts for naphthalene and benzene in various solvents (in cm^{-1}).

	Naphthalene		Benzene		$\frac{\Delta_{FC}\ (\text{Benzene})}{\Delta_{FC}\ (\text{Naphthalene})}$
	Δ_{gl}(a) ($\pm 20\ cm^{-1}$)	Δ_{FC}	Δ_{gl}(b) ($\pm 20\ cm^{-1}$)	Δ_{FC}	
CH_4	-(220)	-	-171	32	
C_2H_6	248	28	247	58	(2.1)
C_3H_8	260	38	270	69	(1.8)
C_2H_4	274	43	253	96	(2.2)
C_3H_6	300	49	279	119	(2.4)
1-C_4H_8	288	61	303	124	(2.0)

(a) naphthalene gas phase 0^o_o absorption at 32020 cm^{-1};
D.P. Craig, J.M. Hollas, M.F. Redies and S.C. Wait, Trans. Roy. Soc. London, A253, 543 (1961).

(b) benzene gas phase 0^o_o absorption at 38289 cm^{-1}, ref. 20.

TABLE III

Decay rate of naphthalene and benzene in various solvents; $k = a + b\,e\frac{\Delta E}{k_B T}$. K is given in units of s^{-1}.

Naphthalene	a	b	ΔE (cm^{-1})
/C_2H_6	2.7×10^6	6.2×10^6	104
/C_3H_6	2.6×10^6	6.8×10^6	95
1-C_4H_8	3.0×10^6	7.2×10^6	114

Benzene	a	b	ΔE (cm^{-1})
C_2H_6 (1 ppm)	5.3×10^6	1.5×10^7	215
(0.3 ppm)	4.2×10^6	3.8×10^6	57
C_3H_8 (1 ppm)	6.5×10^6	2.0×10^7	184
(0.3 ppm)	4.7×10^6	7.1×10^6	86

FIGURE CAPTIONS

Figure 1

Absorption (a) and emission (b) spectra of the first excited singlet state $^1B_{3u}$ of naphthalene (5 ppm) in liquid C_2H_6 at 90K. The assignment of the features is as follows: $\bar{8}^1_0$ at 3100Å, $\bar{7}^1_0$ and $\bar{8}^1_0 9^1_0$ at 3060Å, $\bar{8}^1_0 8^1_0$ and 6^1_0 at 3035A, $\bar{8}^1_0 7^1_0$, 4^1_0 at 3115A, 8^0_1 at 3200Å, and $\bar{8}^0_1$ at 3225Å. The arrow indicates the 0^0_0 at 3147Å. The notation for the modes (barred and unbarred, ref. 19) represents b_{1g} and a_g vibrational symmetry respectively.

Figure 2

Lifetime of naphthalene $^1B_{3u}$ state as a function of temperature in liquid C_2H_4; (X) 0.1 ppm, (0) 1 ppm. (1 ppm = 1.37×10^{-5} mole/ℓ)

Figure 3

Lifetime of naphthalene $^1B_{3u}$ state as a function of temperature in liquid C_2H_6; (X) 0.1 ppm, (0) 0.5 ppm, (Δ) 3.5 ppm. (1 ppm = 1.9×10^{-5} mole/ℓ)

Figure 4

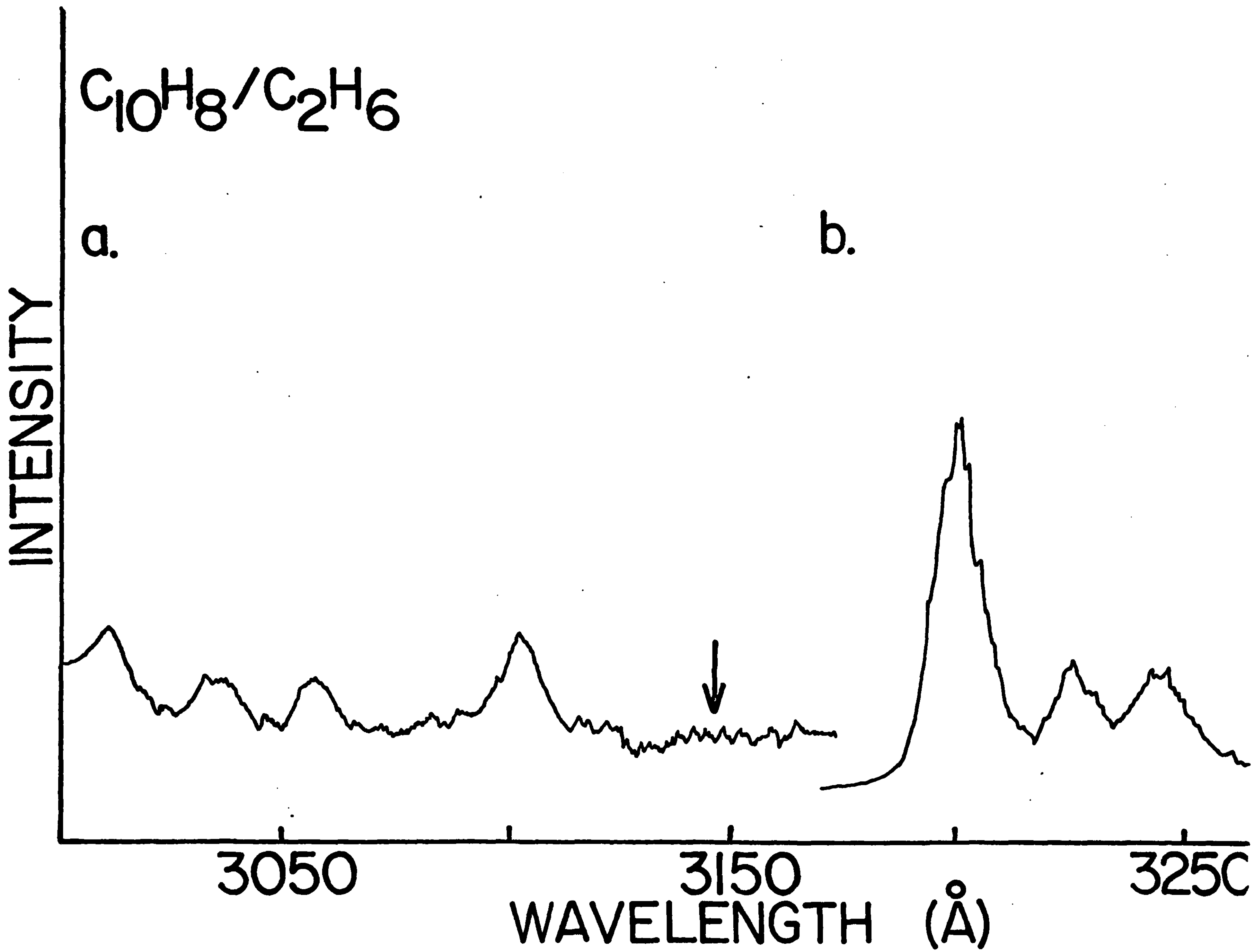
Lifetime of naphthalene $^1B_{3u}$ state as a function of temperatures in liquid 1-C_4H_8; (X) 0.1 ppm, (0) 0.2 ppm, (Δ) 1 ppm, (□) 7 ppm. (1 ppm = 1.06×10^{-5} mole/ℓ)

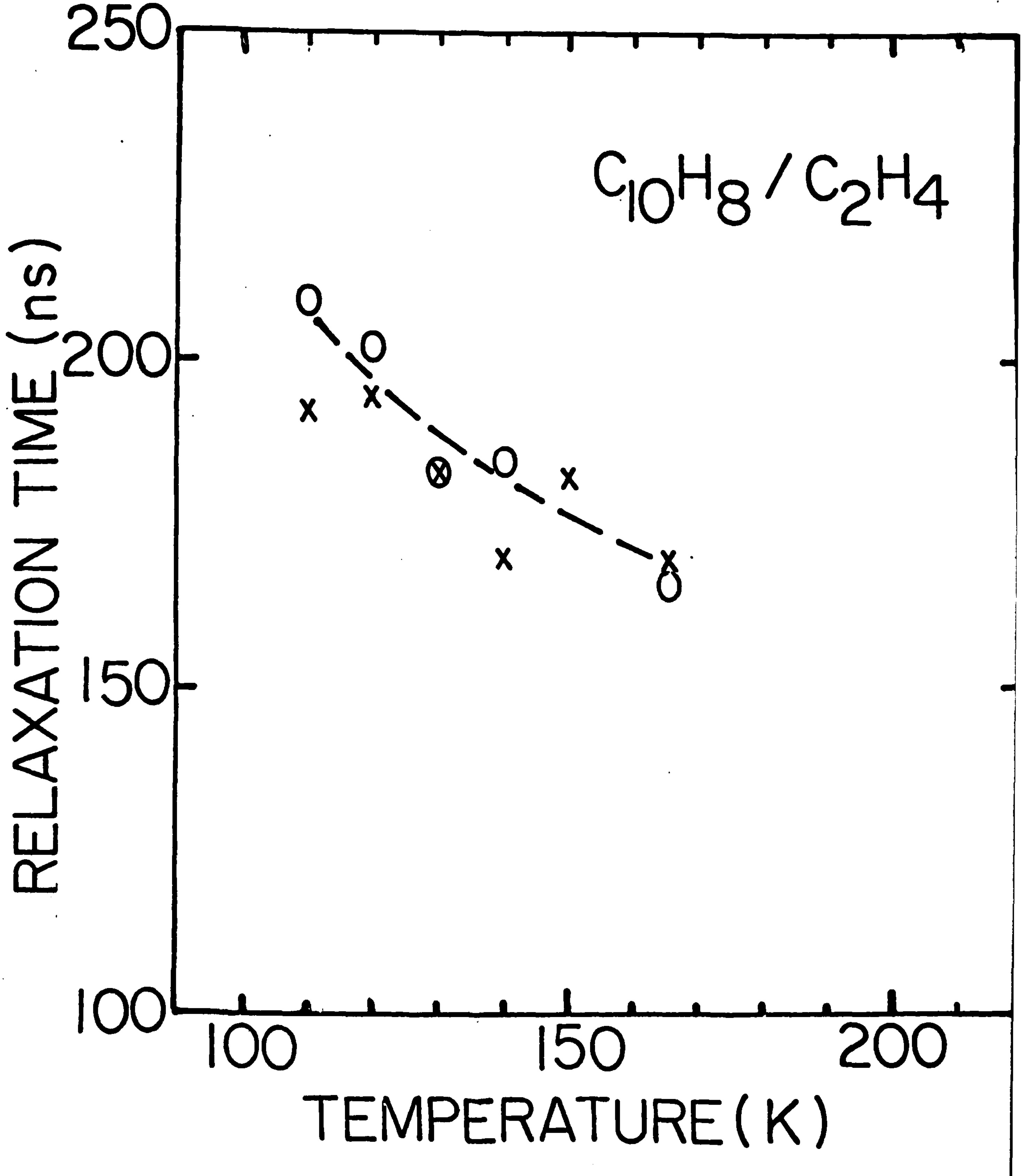
Figure 5

Lifetime of naphthalene $^1B_{3u}$ state as a function of temperature in liquid C_3H_6; (X) 0.1 ppm, (0) 1 ppm, (Δ) 5 ppm. A small increase of lifetime has been observed as temperature increases. At even higher temperatures, the reduction of lifetime indicates a increase competing decay rate from nonradiative process. (1 ppm = 1.23 x 10^{-5} mole/ℓ)

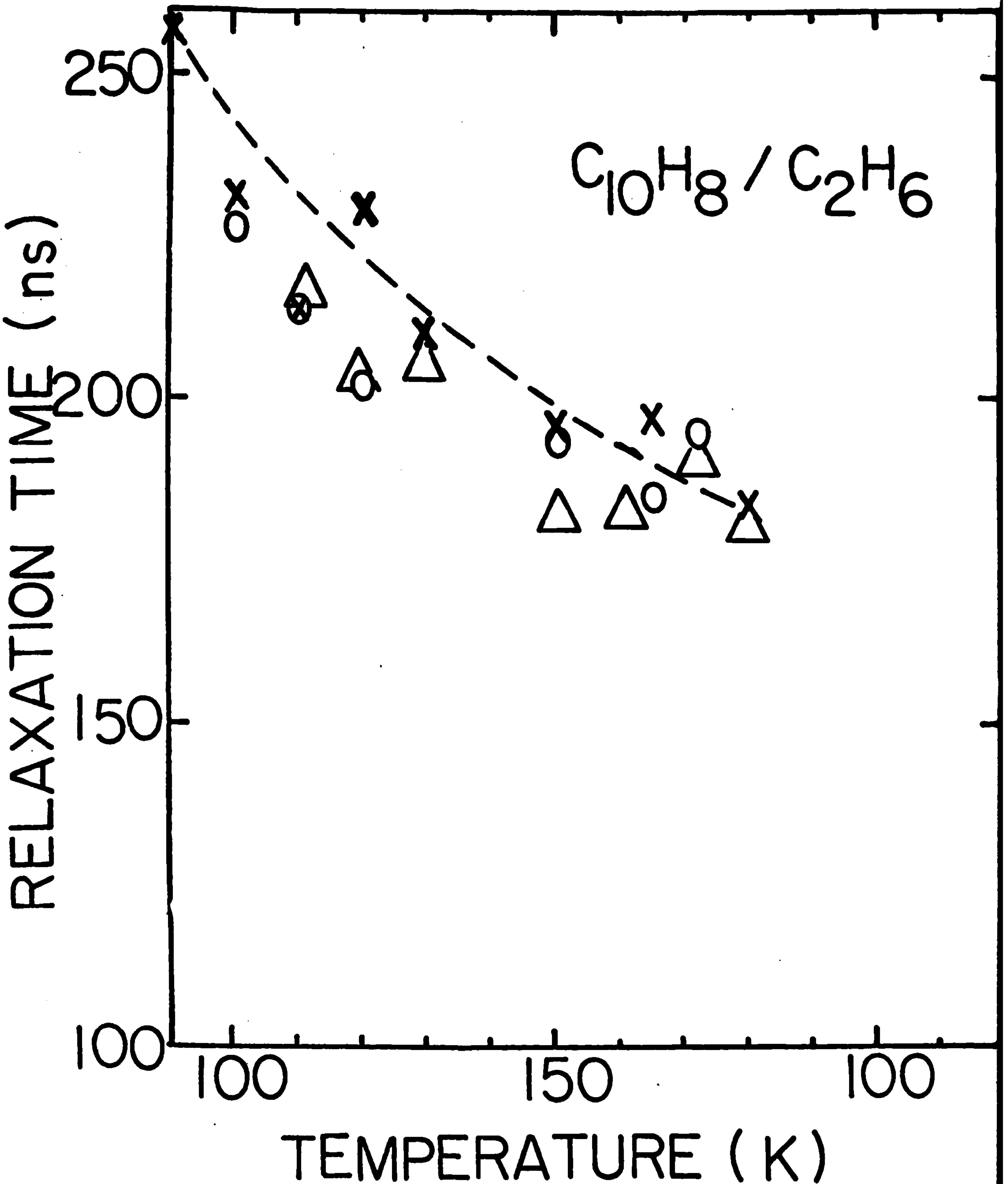
Figure 6

Lifetime of naphthalene $^1B_{3u}$ state as a function of temperature in liquid C_3H_8; (X) 0.1 ppm, (O) 1 ppm. The small values of lifetime are due to a small concentration of impurities in the solvent. Nevertheless, the small increase of lifetime observed at ca. 170K is the result of the breakup of excimer at these higher temperatures. (1 ppm = 1.33 x 10^{-5} mole/ℓ)

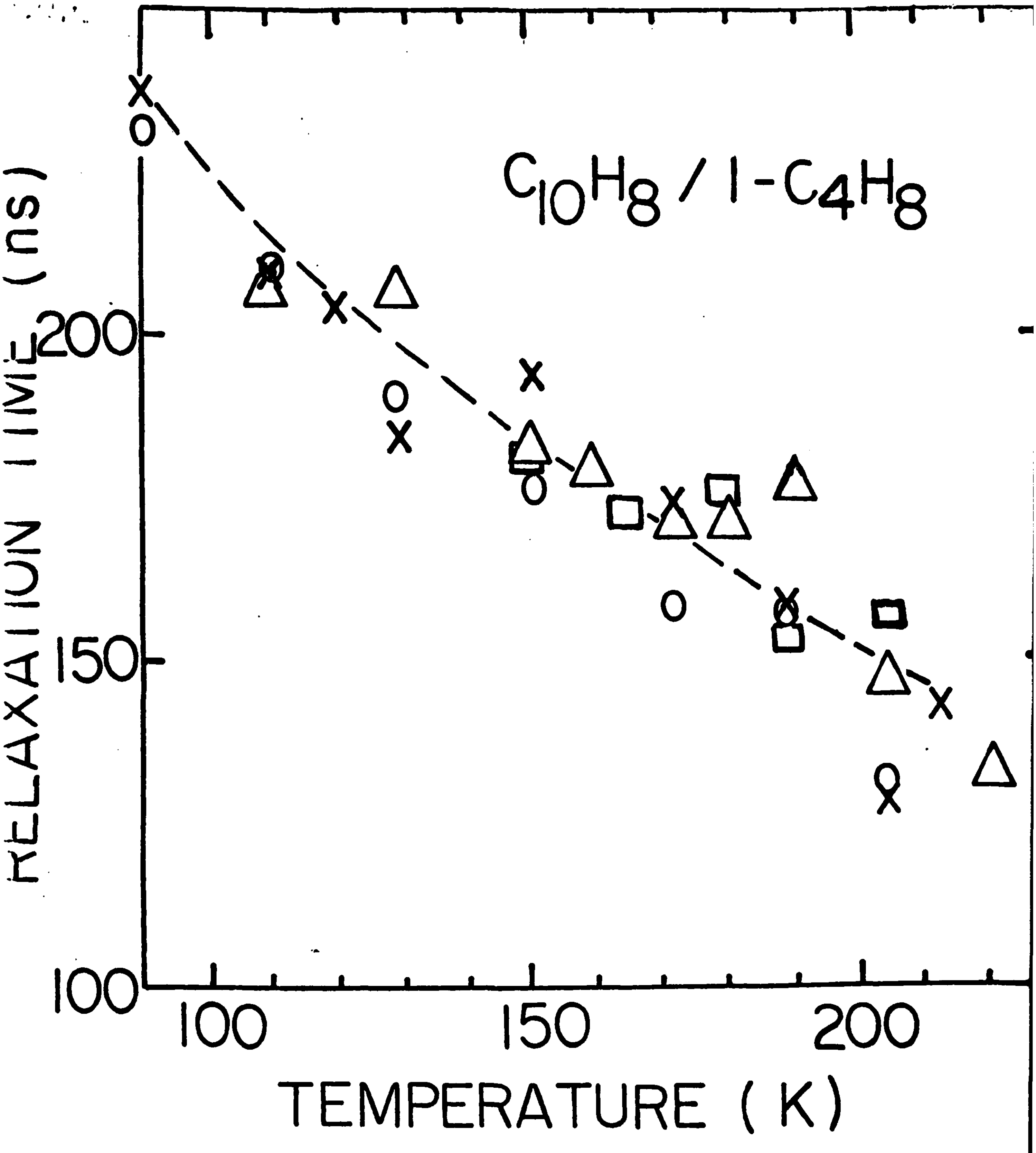

$C_{10}H_8/C_2H_6$
a.
b.
INTENSITY
3050
3150
3250
WAVELENGTH (Å)

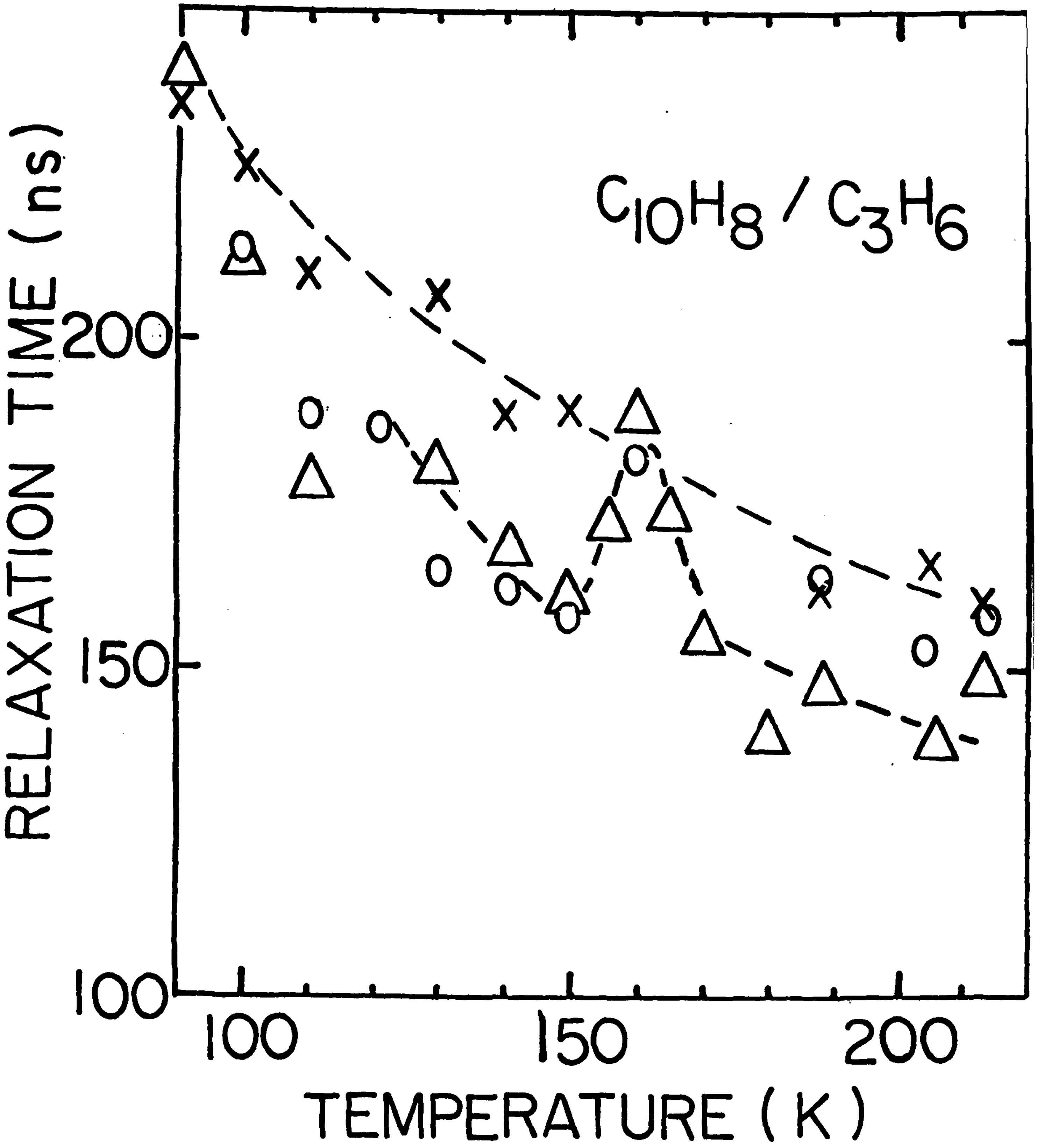


$C_{10}H_8 / C_2H_4$
RELAXATION TIME (ns)
250
200
150
100
100
150
200
TEMPERATURE (K)

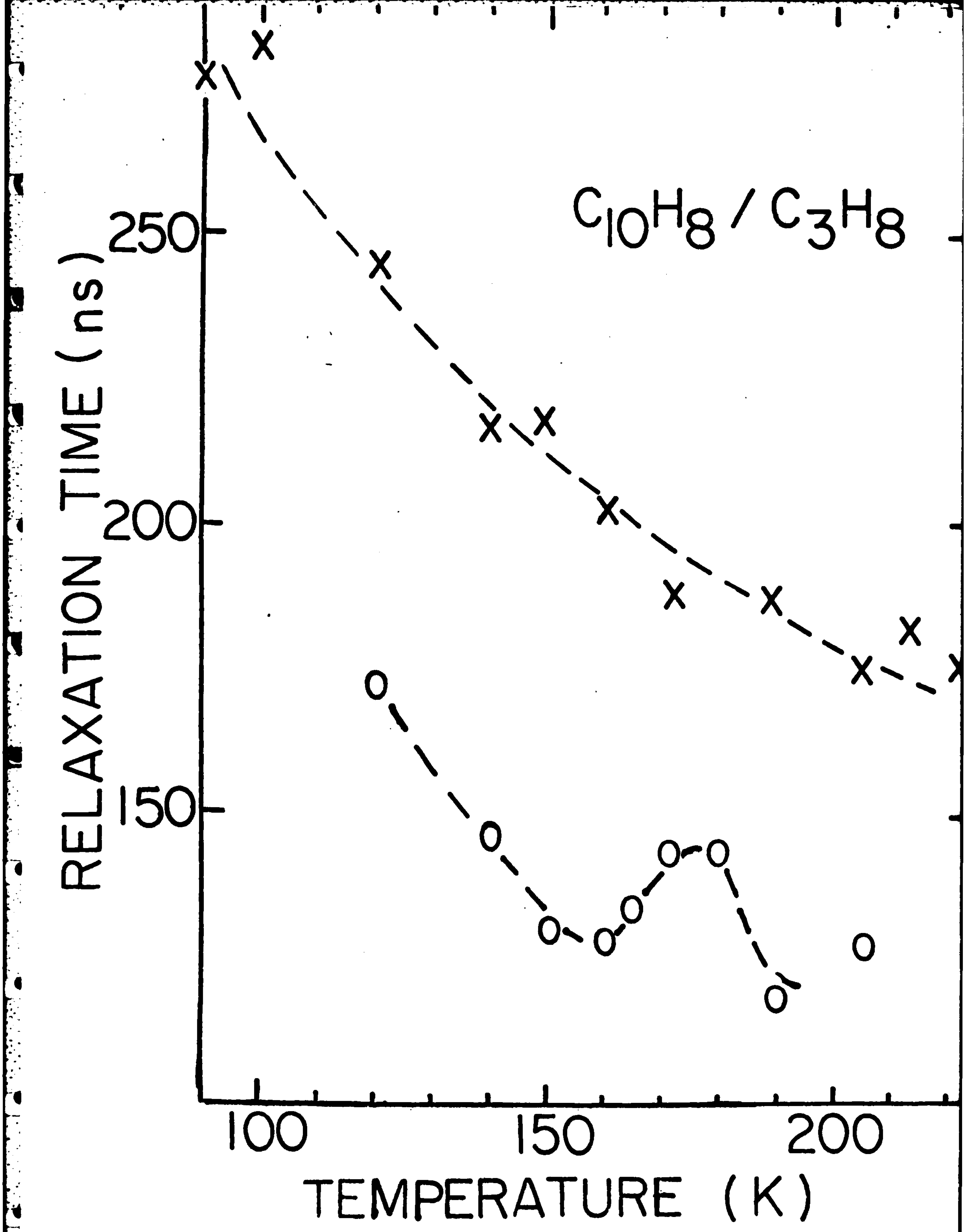


$C_{10}H_8 / C_2H_6$
RELAXATION TIME (ns)
250
200
150
100
TEMPERATURE (K)
100
150
100


$C_{10}H_8 / 1-C_4H_8$
RELAXATION TIME (ns)
100
150
200
TEMPERATURE (K)
100
150
200



RELAXATION TIME (ns)
$C_{10}H_8 / C_3H_6$
200
150
100
100
150
200
TEMPERATURE (K)


$C_{10}H_8 / C_3H_8$
RELAXATION TIME (ns)
250
200
150
100
150
200
TEMPERATURE (K)

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